

- 23 -

WE CLAIM:

1. A method for making polymer-supported metal nanoparticles, comprising:
 - providing a polymer support material;
 - contacting the polymer support with an appropriate metal nanoparticle or metal nanoparticle precursor;
 - contacting the polymer support material and metal or metal precursor with a fluid that swells the polymer support material sufficiently to allow the metal or metal precursor to diffuse into the polymer support material; and
 - if present, reducing the metal precursor to provide a metal nanoparticle.
- 10 2. The method according to claim 1 where the polymer support material is a plastic.
- 15 3. The method according to claim 1 where the polymer support material is a polyalkylene polymer, a substituted polyalkylene polymer, a halogenated polymer, a polyester, or combinations of such materials.
- 20 4. The method according to claim 1 where the polymer support material is polyethylene, polypropylene, polybutylene, poly(4-methyl-1-pentene), poly(tetrafluoroethylene), perfluoroalkyl-tetrafluoroethylene copolymer, polyimide, polybenzimidazole, and combinations of such materials.
- 25 5. The method according to claim 1 where the plastic support material is high density polyethylene, perfluoroalkyl-tetrafluoroethylene copolymer, or combinations thereof.
- 30 6. The method according to claim 1 where the metal or a metal of the metal precursor is palladium, rhodium, platinum, iridium, osmium, gold, nickel, iron or combinations thereof.
7. The method according to claim 1 where the metal nanoparticle comprises an alloy or aggregate of two or more different metals.

- 24 -

8. The method according to claim 1 where the metal precursor includes at least one moiety selected from the group consisting of phosphates, β -diketones, phosphine oxides, dithiocarbamates, crown ethers, and combinations thereof.

5 9. The method according to claim 8 where the moiety is selected from the group consisting of tri-*n*-butylphosphate, tri-*n*-octylphosphate, triphenylphosphate, acetylacetone, trifluoroacetylacetone, hexafluoroacetylacetone, thenoyltrifluoroacetone, heptafluorobutanoylpivaloylmethane, 4, 4-trifluoro-1-(2-thienyl)-1, 3-butanedione, tri-*n*-butylphosphine oxide, tri-*n*-octylphosphine oxide, triphenylphosphine oxide,
10 bis(trifluoroethyl)dithiocarbamate, diethyldithiocarbamate, H-crown, F2-crown, F6-crown, and combinations thereof.

15 10. The method according to claim 6 where the metal precursor comprises Pd(II).

11. The method according to claim 10 where the metal precursor comprises Pd(hfa)₂.

12. The method according to claim 6 where the metal precursor comprises
20 Rh(III).

13. The method according to claim 12 where the metal precursor comprises Rh(acac)₃.

25 14. The method according to claim 1 further comprising contacting the support material in a pressure cell.

15. The method according to claim 1 where the fluid is carbon dioxide, nitrogen, nitrous oxide, methane, ethylene, propane or propylene.

30 16. The method according to claim 1 where the fluid is supercritical.

17. The method according to claim 1 where the fluid is supercritical carbon dioxide.

- 25 -

18. The method according to claim 1 where reducing a metal of the metal nanoparticle precursor comprises contacting the metal precursor with hydrogen.

19. The method according to claim 16 comprising hydrogen reduction at a
5 pressure greater than ambient.

20. The method according to claim 16 where the hydrogen reduction is conducted at a pressure greater than ambient to a pressure of at least 300 atmospheres.

10 21. The method according to claim 1 and further comprising adding a fluid modifier to the fluid.

15 22. The method according to claim 21 where the fluid modifier is selected from the group consisting of lower alkyl alcohols, lower alkyl esters, lower alkyl phosphates, lower alkyl halogenated organic compounds, and combinations thereof.

23. The method according to claim 21 where the fluid modifier is methanol, ethanol, ethyl acetate, tributyl phosphate, methylene chloride, chloroform and combinations thereof.

20 24. The method according to claim 12 further comprising using a catalytic amount of Pd(II) to aid reduction of the Rh(III).

25 25. The method according to claim 12 where the rhodium nanoparticle reduction is performed at a temperature between greater than ambient to at least 300 °C.

26. The method according to claim 1 further comprising removing reaction byproducts by repeated washing with the fluid.

30 27. A method for performing chemical reactions, comprising providing a polymer-supported metal nanoparticles and selected reagents under further providing conditions allowing chemical reactions to occur.

- 26 -

28. The method according to claim 27 where a metal of the metal nanoparticle is palladium, rhodium, platinum, iridium, osmium, gold, nickel, iron or combinations thereof.

5 29. The method according to claim 27 where the metal nanoparticle comprises an alloy or aggregate of two or more different metals.

10 30. The method according to claim 27 where the polymer is a polyalkylene polymer, a substituted polyalkylene polymer, a halogenated polymer, a polyester, or combinations of such materials.

15 31. The method according to claim 27 where the polymer is polyethylene, polypropylene, polybutylene, poly(4-methyl-1-pentene), poly(tetrafluoroethylene), perfluoroalkyl-tetrafluoroethylene copolymer, polyimide, polybenzimidazole, and combinations of such materials.

20 32. The method according to claim 27 where the plastic support material is high density polyethylene, perfluoroalkyl-tetrafluoroethylene copolymer, or combinations thereof.

33. The method according to claim 27 further comprising contacting the metal nanoparticles and/or reagents with a supercritical fluid.

25 34. The method according to claim 27 where the supercritical fluid is supercritical carbon dioxide.

35. The method according to claim 27 where the reaction is a reduction and the reducing agent is hydrogen.

30 36. A method for reducing or oxidizing sites of unsaturation of organic compounds having sites of unsaturation or functional groups capable of being reduced or oxidized, or for performing coupling reactions with organic compounds, comprising:
providing a mixture comprising polymer-supported, metal nanoparticles and one or more organic compounds; and

performing a reduction reaction, an oxidation reaction, a coupling reaction, or combinations of such reactions.

37. The method according to claim 36 where performing comprises contacting
5 the mixture with a reducing agent or an oxidizing agent

38. The method according to claim 36 where a metal of the metal nanoparticle is palladium, rhodium, platinum, iridium, osmium, gold, nickel, iron or combinations thereof.

10 39. The method according to claim 36 where the metal nanoparticle comprises an alloy or aggregate of two or more different metals.

15 40. The method according to claim 36 where the polymer is a polyalkylene polymer, a substituted polyalkylene polymer, a halogenated polymer, a polyester, or combinations of such materials.

20 41. The method according to claim 36 where the polymer is polyethylene, polypropylene, polybutylene, poly(4-methyl-1-pentene), poly(tetrafluoroethylene), perfluoroalkyl-tetrafluoroethylene copolymer, polyimide, polybenzimidazole, and combinations of such materials.

25 42. The method according to claim 36 where the plastic support material is high density polyethylene, perfluoroalkyl-tetrafluoroethylene copolymer, or combinations thereof.

43. The method according to claim 36 further comprising contacting the mixture with a supercritical fluid.

30 44. The method according to claim 43 where the supercritical fluid is supercritical carbon dioxide.

45. The method according to claim 37 where the reducing agent is hydrogen.

35 46. The method according to claim 44 where the reducing agent is hydrogen.

47. The method according to claim 45 and further comprising conducting a reduction reaction at a temperature between greater than ambient to at least 300 °C.

5 48. The method according to claim 47 where the reaction temperature is about 50 °C.

10 49. The method according to claim 36 where contacting comprises contacting with hydrogen gas at a pressure greater than ambient and contacting with supercritical carbon dioxide.

50. The method according to claim 49 comprising contacting with hydrogen at a pressure of greater than ambient to at least about 10 atmospheres.

15 51. The method according to claim 36 where the organic compound is an olefin and the reaction is a reduction of an olefinic moiety.

52. The method according to claim 36 where the organic compound is an arene and the reaction is a reduction of at least one site of unsaturation.

20 53. The method according to claim 52 where the arene is a halogenated arene.

54. The method according to claim 36 where the organic compound is an arene having an oxygen-bearing functional group, a nitrogen-bearing functional group, or both.

25 55. The method according to claim 52 where the arene has 20 or fewer carbon atoms.

30 56. The method according to claim 52 where the arene is selected from the group consisting of benzene, naphthalene, anthracene, phenanthrene, halogenated benzene, halogenated naphthalene, halogenated anthracene, halogenated phenanthrene, or combinations thereof.

- 29 -

57. The method according to claim 56 where the metal of the metal nanoparticle is selected from the group consisting of palladium, rhodium, and mixtures thereof.

5 58. The method according to claim 57 where the polymer support material is selected from the group consisting of high density polyethylene and perfluoroalkyl-tetrafluoroethylene copolymer.

10 59. The method according to claim 36 where the metal nanoparticle is palladium or rhodium, the organic compound is benzene or halogenated benzene and cyclohexane is produced as a hydrogenation product.

15 60. The method according to claim 36 where the metal nanoparticle is palladium, the unsaturated hydrocarbon is naphthalene or halogenated naphthalene, and tetralin or decalin is produced as a hydrogenation product.

20 61. The method according to claim 36 where plural reduction products are produced, and relative amounts of the reduction products can be varied by selecting an appropriate metal nanoparticle, polymer support material, or both.

25 62. The method according to claim 61 where the organic compound is phenol, the metal nanoparticle is palladium, the polymer support material is high density polyethylene, and cyclohexanone and cyclohexanol are produced in about 78% and 6% yield, respectively.

63. The method according to claim 61 where the organic compound is phenol, the metal nanoparticle is palladium, the polymer support material is perfluoroalkyl-tetrafluoroethylene copolymer, and cyclohexanone and cyclohexanol are produced in about 62% and 38% yield, respectively.

30 64. The method according to claim 36 where the organic compound includes a nitro group.

35 65. The method according to claim 64 where the organic compound is nitrobenzene, and aniline is produced by hydrogenation.

66. The method according to claim 36 where the organic compound is halogenated.

5 67. The method according to claim 66 where the organic compound is a chlorinated aromatic compound

68. The method according to claim 67 where the reducing agent is hydrogen and a dehalohydrogenation reaction occurs.

10 69. The method according to claim 67 where the chlorinated aromatic compound is chlorophenol, the metal nanoparticle is palladium, the polymer support is perfluoroalkyl-tetrafluoroethylene copolymer, high density polyethylene, or combinations thereof.

15 70. The method according to claim 69 where reduction reaction products include cyclohexanone, cyclohexanol, cyclohexane, phenol and benzene:

20 71. The method according to claim 70 where cyclohexanone is produced in about a 70% or greater yield.

72. The method according to claim 67 where the chlorinated aromatic compound is a chlorinated benzene compound, and the metal nanoparticle is palladium.

25 73. The method according to claim 72 comprising continuing a reduction reaction for a time period sufficient to produce cyclohexane as a primary reaction product.

74. The method according to claim 73 where the time period is about 1 hour.

30 75. The method according to claim 72 comprising continuing a reduction reaction for a time period sufficient to produce a mixture of cyclohexane and benzene as primary reaction products.

35 76. The method according to claim 75 where the time period is about 30 minutes.

77. The method according to 67 where the chlorinated aromatic compound is a chlorinated biphenyl.

5 78. The method according to 67 where the chlorinated aromatic compound is a chlorinated phenol.

79. The method according to claim 78 where the chlorinated phenol is 2,4-dichlorophenol.

10 80. The method according to claim 79 where the metal nanoparticle is palladium, the polymer support is perfluoroalkyl-tetrafluoroethylene copolymer and primary reaction products are a substantially equal mixture of cyclohexanone and cyclohexanol.

15 81. The method according to claim 79 where the metal nanoparticle is rhodium, the polymer support is perfluoroalkyl-tetrafluoroethylene copolymer and primary reaction products are cyclohexanone, cyclohexanol, and cyclohexane.

20 82. A method for reducing unsaturation in organic compounds having sites of unsaturation or functional groups capable of being reduced, comprising:
providing a mixture comprising polymer-supported metal nanoparticles and the organic compound; and
contacting the mixture with a reducing agent.

25 83. The method according to claim 82 where the reducing agent is hydrogen.

84. The method according to claim 82 where the metal nanoparticle is an alloy or aggregate of two or more different metals.